

# Effect of lithium difluoro(oxalato)borate (LiDFOB) additive on the performance of high-voltage lithium-ion batteries

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**Abstract** Lithium difluoro(oxalato)borate (LiDFOB) was investigated as an electrolyte additive for high-voltage lithium-ion batteries in order to decrease the decomposition of the electrolyte. As a typical high-voltage cathode material,  $\text{LiCoPO}_4$  was tested in the LiDFOB-containing electrolyte, exhibiting higher reversible charge/discharge capacity and better cyclic stability. The effect of LiDFOB on the formation of a stable interphase film was investigated through cyclic voltammetry and X-ray photoelectron spectroscopy. LiDFOB was helpful to form a stable interphase film and passivate the cathode surface; therefore, the decomposition of the electrolyte was inhibited accordingly.

**Keywords** Lithium-ion batteries · LiDFOB · Electrolyte additive · High voltage

## 1 Introduction

Lithium-ion batteries (LIBs) have been employed in various electronic devices; however, the energy and power density cannot meet the demand for electric vehicles (EVs) and hybrid EVs (HEVs) [1–3]. To increase the energy and power density of LIBs, one appropriate way is the application of cathode materials with high electrode potentials, such as  $\text{LiCoPO}_4$  (LCP) with the electrode potential of nearly 5 V vs.  $\text{Li/Li}^+$ . However, conventional electrolytes based on organic carbonate solvents will be oxidized at about 4.5 V [4], and also transition-metal ions in cathode

materials can catalyze the oxidation reaction and accelerate the decomposition of the electrolytes [5]. Among the explorations on high-voltage electrolytes, rather attention has been paid to room temperature ionic liquids (RTILs) [6–8], which exhibit wide electrochemical windows, low flammability and volatility. However, the disadvantages of high viscosity and low ionic conductivity lead to poor cyclic stability and rate performance [9]. Several modification methods, such as mixing organic solvents with RTILs [10, 11] and adding additives to assist in forming stable solid electrolyte interface (SEI) films [8, 12], have been proposed to promote the application of RTILs. Sulfones and nitriles also have wide electrochemical windows and have been investigated as the electrolyte solvents for high-voltage LIBs [13–19]. However, the performances are not satisfactory yet.

The introduction of additives to the conventional electrolytes may be a feasible way at the current stage [20, 21]. It has been reported that some specific additives will decompose under high voltages ahead of electrolyte components and assist in the formation of protective films to passivate the surface of cathode materials [5, 22], and then the decomposition of the electrolytes can be inhibited accordingly.

Lithium difluoro(oxalato)borate (LiDFOB) was first proposed by Zhang [23] as a new lithium salt for LIBs, with the advantages of both  $\text{LiBF}_4$  and lithium bisoxalatoborate (LiBOB). LiDFOB can assist in forming stable SEI films on graphite anodes [24], and improve the electrochemical performance [25–27], thermal stability [28], and cyclic performance at elevated temperatures [29]. Moreover, the assistance of LiDFOB in forming better interphase films on cathodes has been identified [30]. However, the effect of LiDFOB on high-voltage cathode materials is still unknown.

In this study,  $\text{LiCoPO}_4$ , as a representative of high-voltage cathode materials, was prepared [31]. Since

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LiCoPO<sub>4</sub> always presented poor cyclic stability due to the electrolyte decomposition at high potentials and its intrinsic properties, such as the low electronic conductivity and structural instability during Li deintercalation [32, 33], even though various modified strategies were employed [13, 32–51]. The effect of LiDFOB on high-voltage cathode materials can be disclosed distinctly in this system.

## 2 Experimental

### 2.1 Preparation of LiCoPO<sub>4</sub> samples

LiCoPO<sub>4</sub> was prepared via a sol–gel route [31]. A stoichiometric mixture of LiNO<sub>3</sub>, Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and citric acid was dissolved in deionized water with magnetic stirring, and then (NH<sub>4</sub>)<sub>2</sub>HPO<sub>4</sub> in stoichiometric ratio was added to the solution and stirred at 85 °C to remove the excessive water. The gel was dried at 100 °C in air. The precursor was heated at 350 °C for 2 h in flowing argon. The mixture was ground, pressed into pellets and heated for 6 min by microwave at 800 W, and then the mixture was heated at 500 °C for 4 h in air.

### 2.2 Preparation of electrolytes

LiDFOB was synthesized as previously described [23]. A stoichiometric mixture of BF<sub>3</sub>·Et<sub>2</sub>O and Li<sub>2</sub>C<sub>2</sub>O<sub>4</sub> was loaded into a Teflon-lined stainless steel autoclave. The autoclave was sealed and heated at 80 °C for 24 h. The obtained solid–liquid mixture was purified by suction filtration, rotary evaporation and recrystallization. All the experiments were performed in a dry environment. The synthesized LiDFOB was dried in vacuum at 130 °C for 24 h. The standard electrolyte was 1 mol L<sup>−1</sup> LiPF<sub>6</sub> dissolved in a mixture of ethylene carbonate (EC), propylene carbonate (PC) and ethyl methyl carbonate (EMC) (1:1:3 by volume). The optimized electrolyte was prepared by mixing the standard electrolyte with 5 wt% LiDFOB and stirring for 24 h in an argon-filled glove box.

### 2.3 Material characterization

The samples were characterized by X-ray diffraction (XRD, D/MAX III diffractometer with Cu-Kα radiation, λ = 1.5418 Å). Surface analysis of the cathodes was taken after the cells completed 40 charge/discharge cycles. The cathode films of the cells were taken out and washed with anhydrous ethanol for three times and dried at 100 °C for 24 h in vacuum to remove the residual electrolytes. Surface element analysis was performed by X-ray photoelectron spectroscopy (XPS, Axis Ultra DLD, Kratos Analytical Ltd.).

### 2.4 Cell assembly and electrochemical tests

The cathode was prepared with LiCoPO<sub>4</sub>, acetylene black, and polytetrafluoroethylene (PTFE) binder with a weight ratio of 75:20:5. Metallic Li foil was used as the anode. LiCoPO<sub>4</sub>/electrolyte/lithium test cells with two different electrolytes were assembled in an argon-filled glove box. Galvanostatic charge/discharge tests were performed on a Land CT2001 battery tester between 3.0 and 5.1 V at room temperature. Cyclic voltammetry (CV) was performed on a Zahner-Elektrik IM6e electrochemical workstation in a potential range of 3.0–5.3 V at a scan rate of 0.1 mV s<sup>−1</sup>.

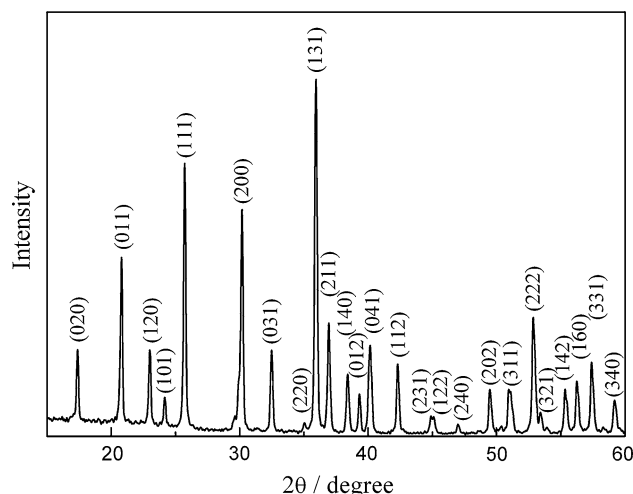
## 3 Results and discussion

### 3.1 Phase confirmation

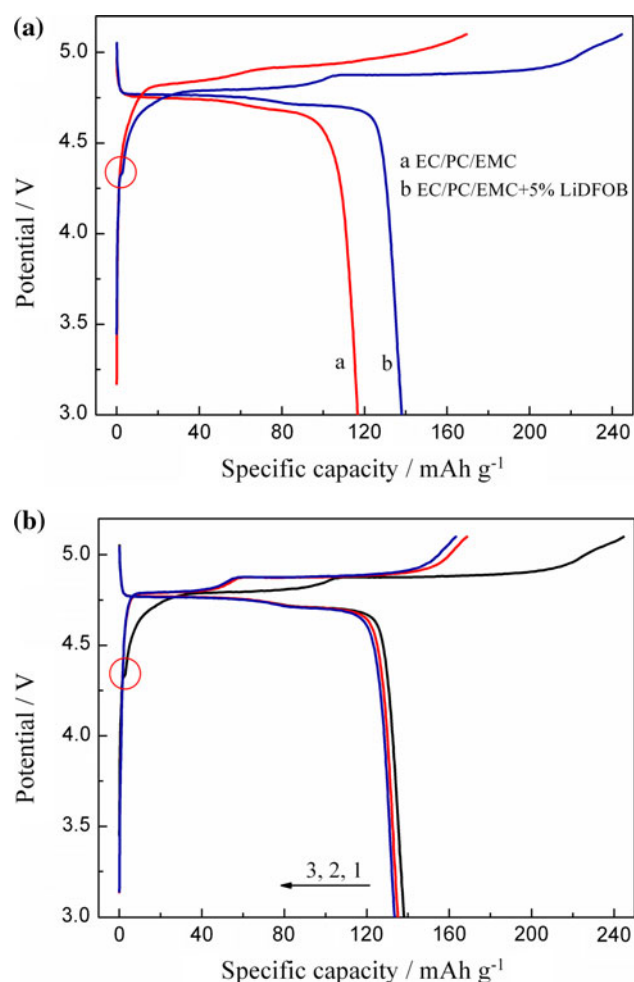
The XRD patterns of LiCoPO<sub>4</sub> samples are shown in Fig. 1. The samples are well crystallized, and all diffraction peaks are indexed in the *Pmnb* space group without impurity phases. Since the high-power microwave heating is profitable for crystallization, the LiCoPO<sub>4</sub> samples exhibit high peak intensity even though the heating temperature was as low as 500 °C.

### 3.2 Charge/discharge measurements

After the addition of LiDFOB to the electrolyte, the electrochemical performance was remarkably improved. The initial galvanostatic charge/discharge curves are shown in Fig. 2a for the LiCoPO<sub>4</sub> test cells with or without LiDFOB additive, measured at a 0.1 C rate. Two plateaus are observed in all curves, which are attributed to the two-step mechanism [52]. Moreover, a short plateau at 4.35 V is

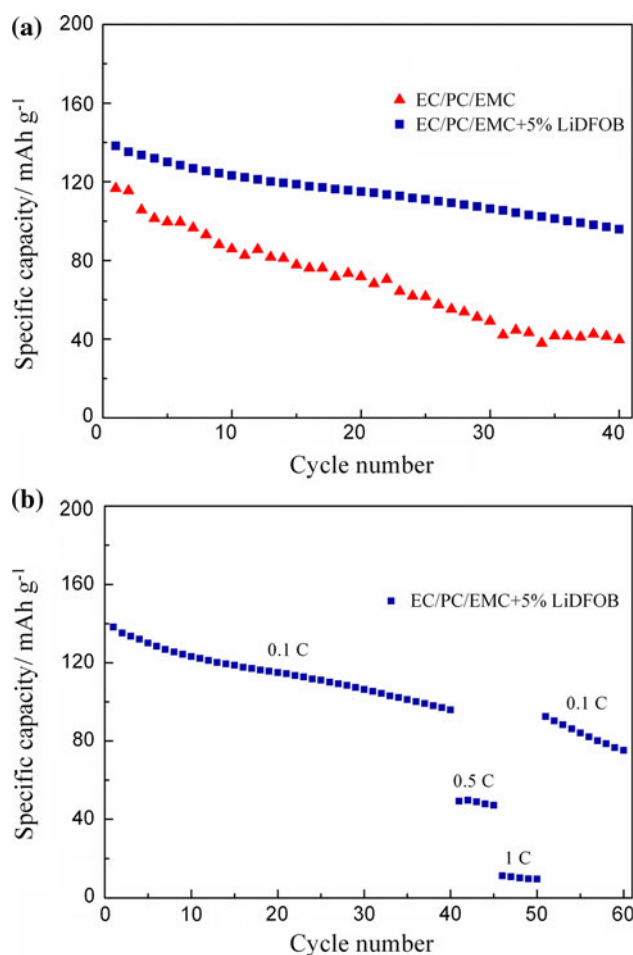


**Fig. 1** XRD patterns of LiCoPO<sub>4</sub> samples



**Fig. 2** Initial charge/discharge curves of LiCoPO<sub>4</sub> in the electrolytes with or without LiDFOB (a); initial three-cycle charge/discharge curves of LiCoPO<sub>4</sub> only in the LiDFOB-containing electrolyte (b)

observed in the charge curve of LiCoPO<sub>4</sub> in the LiDFOB-containing electrolyte. The plateau is due to the decomposition of LiDFOB, and then higher charge capacity is obtained. The addition of LiDFOB also resulted in a higher capacity of 138.2 mAh g<sup>-1</sup>, while the discharge capacity of LiCoPO<sub>4</sub> was only 116.7 mAh g<sup>-1</sup> in the electrolyte without LiDFOB. From Fig. 2a the decrease of electrode polarization can be seen obviously due to the addition of LiDFOB. The continuous decomposition of the electrolyte on the cathode surface increases the electrode polarization. After the addition of LiDFOB, the decomposition products of LiDFOB participate in the formation of a more stable interphase film (see the following XPS results), which restricts the electrode polarization. Figure 2b shows the charge/discharge curves for the initial three cycles. After the first cycle, the plateau at 4.35 V disappeared, indicating that the decomposition of LiDFOB mainly occurred in the first charge process. The decomposition products inhibit the further decomposition of LiDFOB, and also other



**Fig. 3** Cyclic performance of LiCoPO<sub>4</sub> in the electrolytes with or without LiDFOB at 0.1 C rate (a) and different rates (b)

compositions in the electrolyte. The charge/discharge plateaus become stable after the first cycle.

The cyclic performances are compared in Fig. 3a for LiCoPO<sub>4</sub> electrodes in two different electrolytes. After 40 cycles, the capacity retention is 69.4 % for LiCoPO<sub>4</sub> cycled in the LiDFOB-containing electrolyte, compared with 34.0 % for LiCoPO<sub>4</sub> in the conventional electrolyte. The cells were also cycled at higher rates after 40 cycles, and the performances are shown in Fig. 3b. When the rates were 0.5 and 1 C, the capacities of LiCoPO<sub>4</sub> in the LiDFOB-containing electrolyte were 49.3 and 11.2 mAh g<sup>-1</sup>, respectively. When the rate returned to 0.1 C, the capacity recovered to 92.6 mAh g<sup>-1</sup>, while there was no capacity for LiCoPO<sub>4</sub> in the conventional electrolyte. The results indicate that the addition of LiDFOB to the electrolyte improves the cyclic stability of the test cells. LiDFOB decomposes under high voltage and passivates the LiCoPO<sub>4</sub> surface with a stable interphase film. Therefore, the catalytic decomposition of the electrolyte by the transition-metal ions is inhibited, and high cyclic stability can be achieved. However,

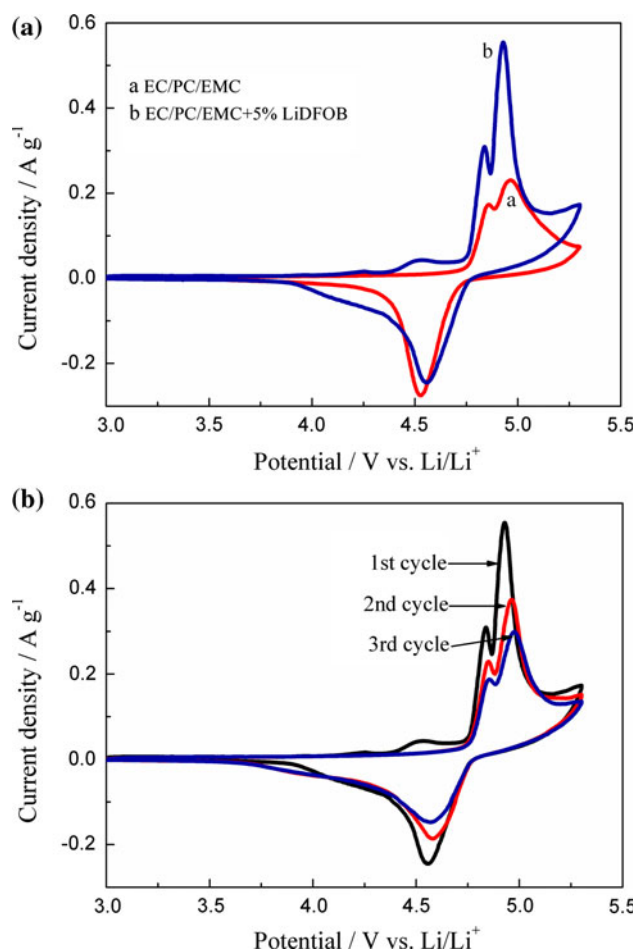
the rate performance is still poor for  $\text{LiCoPO}_4$  even in the LiDFOB-containing electrolyte, compared with other common cathode materials due to its intrinsic properties [31, 32].

To obtain better rate performance, the efforts on the structural modification of  $\text{LiCoPO}_4$  cathode are as important as the electrolyte optimization. Carbon coating is an effective method. However, it is difficult to coat  $\text{LiCoPO}_4$  with carbon uniformly by conventional methods because of the surface properties of  $\text{LiCoPO}_4$  [47]. Also, the studies on the electrolytes that matched with high-voltage  $\text{LiCoPO}_4$  were very limited. Wolfenstine et al. prepared  $\text{LiCoPO}_4$  containing 0.9 wt% carbon and tested the cathodes in the electrolyte based on  $\text{LiPF}_6$  and tetramethylene sulfone. The capacity decreased from 101 to 54  $\text{mAh g}^{-1}$  after 20 cycles [32]. Better performances could be achieved by the combination of  $\text{LiCoPO}_4$  modification and electrolyte optimization. Liu et al. prepared nanoporous microspheres consisting of  $\sim 70$  nm sized carbon-coated  $\text{LiCoPO}_4$  primary particles by spray pyrolysis method and cycled in the LiBOB-containing electrolyte. The capacity was 123  $\text{mAh g}^{-1}$  with a capacity

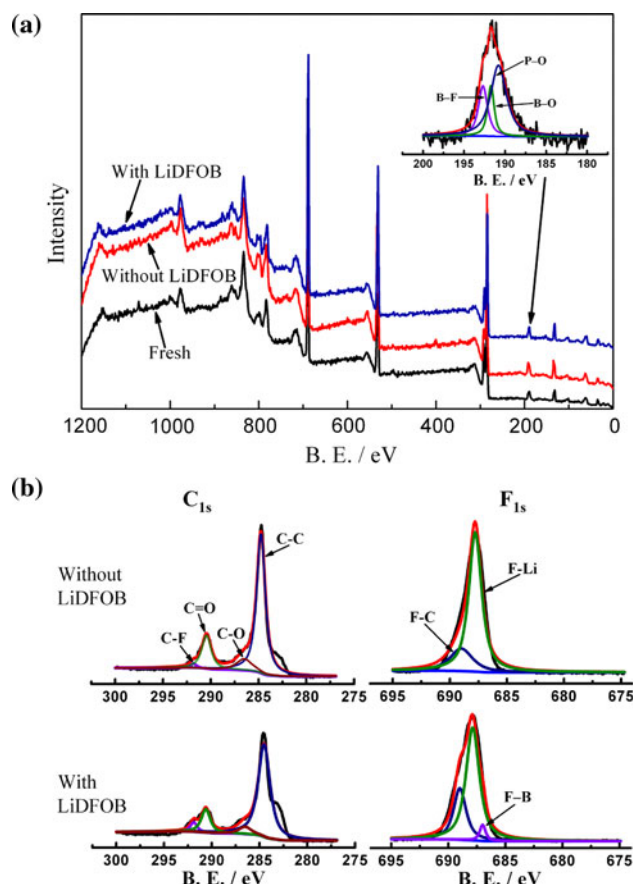
retention of 95 % over 20 cycles [40]. However, the effect of LiBOB was not discussed in detail. In a very recent report, the combination of the network structure  $\text{LiCoPO}_4/\text{C}$  composites and the thiophene addition to the conventional electrolyte resulted in a discharge capacity of 92.8  $\text{mAh g}^{-1}$  and a capacity retention of 68 % after 20 cycles [31]. In this study, the performance of even pure  $\text{LiCoPO}_4$  was greatly improved due to the addition of LiDFOB to the electrolyte. Therefore, electrolytes are still worth extensive investigations for high-voltage LIB cathode materials.

### 3.3 CV tests

The addition of LiDFOB improves the electrochemical reaction activity and reversibility of the cathodes. Figure 4a shows the CV curves of  $\text{LiCoPO}_4$  in the electrolytes with or without LiDFOB. Two anode peaks around 4.9 V are observed from both curves, which are due to the two-step mechanism [52]. In addition, a small peak starting at 4.35 V appears due to the decomposition of LiDFOB. All the peaks are consistent with the initial galvanostatic charge/discharge curves (Fig. 2a). Higher current density appears after the addition of LiDFOB to the electrolyte. Moreover, the



**Fig. 4** Cyclic voltammograms of  $\text{LiCoPO}_4$  in the electrolytes with or without LiDFOB at the initial cycle (a) and only in the LiDFOB-containing electrolyte for the initial three cycles (b)



**Fig. 5** XPS (a) and  $\text{C}_{1s}$  and  $\text{F}_{1s}$  spectra (b) of the fresh and cycled  $\text{LiCoPO}_4$  cathodes in the electrolytes with or without LiDFOB

**Table 1** Surface concentration of the elements in the fresh and cycled LiCoPO<sub>4</sub> cathodes in the electrolytes with or without LiDFOB

	C	O	F	P	Co	B
Fresh cathodes	41.48	15.48	27.07	5.72	10.24	0.00
Cycled cathodes in electrolyte without LiDFOB	38.91	19.88	23.17	7.88	10.16	0.00
Cycled cathodes in electrolyte with LiDFOB	39.95	19.67	21.63	12.26	4.11	2.37

potential differences between the anode and the corresponding cathode peaks decrease simultaneously, representing better electrochemical reversibility compared with LiCoPO<sub>4</sub> in the conventional electrolyte. After the first cycle, the peak at 4.35 V disappears (Fig. 4b), indicating the irreversible decomposition of LiDFOB in the first cycle, and then the decomposition is inhibited by the stable interphase film.

### 3.4 Surface XPS analysis

Figure 5a shows the XPS results of the fresh and cycled LiCoPO<sub>4</sub> cathode films in the electrolytes with or without LiDFOB. Little difference can be observed from the whole spectra. However, for the peaks around 191.5 eV, the cathodes cycled in the LiDFOB-containing electrolyte exhibit a doublet (see the inset of Fig. 5a), which represents the overlapping of B<sub>1s</sub> and P<sub>1s</sub> spectra. After the peak-differentiation-imitating, a peak for P–O (190.8 eV) is observed, and the two peaks for B–O (191.7 eV) and B–F (192.7 eV) belong to the decomposition products of LiDFOB in the interphase film. From the C<sub>1s</sub> spectra in Fig. 5b, two peaks at 291.8 eV (C–F) and 284.8 eV (C–C) are observed, which belong to PTFE and carbon. The two peaks at 290.4 eV (C=O) and 286.4 eV (C–O) are due to the decomposition of the carbonate solvents on the cathode surface. From the F<sub>1s</sub> spectra, the peak at 689.4 eV belongs to PTFE, while the peak for F–Li (688 eV) is due to the decomposition of LiPF<sub>6</sub>. After the addition of LiDFOB, a new peak for F–B bond at 686.9 eV appears, forming from the decomposition of LiDFOB.

The surface concentrations of the elements are shown in Table 1. Compared with the fresh cathodes, the cycled cathodes have lower F and Co content, because the interphase film was generated on the cathode surface during the cycles. Moreover, LiDFOB decomposes to help the formation of a more stable surface film. Therefore, the cathodes cycled in the LiDFOB-containing electrolyte demonstrate the lowest content of F and Co. Besides, the B content is in agreement with the XPS spectra (Fig. 5a), certifying the participation of LiDFOB in the formation of a stable interphase film.

## 4 Conclusion

In summary, for the purpose of inhibiting the decomposition of the electrolyte, LiDFOB was investigated as an

electrolyte additive for high-voltage LIBs. The high-voltage LiCoPO<sub>4</sub> electrode showed better cyclic performance in the LiDFOB-containing electrolyte. LiDFOB decomposed at 4.35 V vs. Li/Li<sup>+</sup> and assisted in forming a stable interphase film, which passivated the cathode surface and decreased the catalytic decomposition of the electrolyte by the transition-metal ions. Therefore, the electrochemical performance was improved by the addition of LiDFOB to the electrolyte. LiDFOB proves a promising Li salt additive for the electrolytes of high-voltage Li ion batteries.

## References

- Armand M, Tarascon JM (2008) *Nature* 451:652
- Arico AS, Bruce P, Scrosati B, Tarascon JM, Van Schalkwijk W (2005) *Nat Mater* 4:366
- Su LW, Jing Y, Zhou Z (2011) *Nanoscale* 3:3967
- Xu K (2004) *Chem Rev* 104:4303
- Li Y, Markmaitree T, Lucht BL (2011) *J Power Sources* 196:2251
- Lewandowski A, Świdarska-Moczek A (2009) *J Power Sources* 194:601
- Borgel V, Markevich E, Aurbach D, Semrau G, Schmidt M (2009) *J Power Sources* 189:331
- Jin J, Li HH, Wei JP, Bian XK, Zhou Z, Yan J (2009) *Electrochim Commun* 11:1500
- Lalia BS, Yoshimoto N, Egashira M, Morita M (2010) *J Power Sources* 195:7426
- Diaw M, Chagnes A, Carré B, Willmann P, Lemordant D (2005) *J Power Sources* 146:682
- Guerfi A, Dontigny M, Charest P, Petitclerc M, Lagacé M, Vijh A, Zaghbi K (2010) *J Power Sources* 195:845
- An YX, Zuo PJ, Cheng XQ, Liao LX, Yin GP (2011) *Electrochim Acta* 56:4841
- Amine K, Yasuda H, Yamachi M (2000) *Electrochim Solid State Lett* 3:178
- Xu K, Angell CA (2002) *J Electrochem Soc* 149:920
- Watanabe Y, Kinoshita S, Wada S, Hoshino K, Morimoto H, Tobishima S (2008) *J Power Sources* 179:770
- Abouimrane A, Belharouak I, Amine K (2009) *Electrochim Commun* 11:1073
- Sun XG, Angell CA (2009) *Electrochim Commun* 11:1418
- Abu-Lebdeh Y, Davidson I (2009) *J Electrochem Soc* 156:60
- Nagahama M, Hasegawa N, Okada S (2010) *J Electrochem Soc* 157:748
- Zhang SS (2006) *J Power Sources* 162:1379
- von Cresce A, Xu K (2011) *J Electrochem Soc* 158:337
- Abe K, Ushigoe Y, Yoshitake H, Yoshio M (2006) *J Power Sources* 153:328
- Zhang SS (2006) *Electrochim Commun* 8:1423
- Zhang SS (2007) *J Power Sources* 163:713



25. Liu J, Chen ZH, Busking S, Amine K (2007) *Electrochem Commun* 9:475
26. Liu J, Chen ZH, Busking S, Belharouak I, Amine K (2007) *J Power Sources* 174:852
27. Li J, Xie KY, Lai YQ, Zhang ZA, Li FQ, Hao X, Chen XJ, Liu YX (2010) *J Power Sources* 195:5344
28. Chen ZH, Qin Y, Liu J, Amine K (2009) *Electrochem Solid State Lett* 12:69
29. Xu MQ, Zhou L, Hao LS, Xing LD, Li WS, Lucht BL (2011) *J Power Sources* 196:6794
30. Fu MH, Huang KL, Liu SQ, Liu JS, Li YK (2010) *J Power Sources* 195:862
31. Xing LY, Hu M, Tang Q, Wei JP, Qin X, Zhou Z (2012) *Electrochim Acta* 59:172
32. Rabanal ME, Gutierrez MC, Alvarado FG, Gonzalo EC, Arroyo-de Dompablo ME (2006) *J Power Sources* 160:523
33. Eftekhari A (2004) *J Electrochem Soc* 151:1456
34. Xie J, Imanishi N, Zhang T, Hirano A, Takeda Y, Yamamoto O (2009) *J Power Sources* 192:689
35. Wolfenstine J, Lee U, Poesse B, Allen JL (2005) *J Power Sources* 144:226
36. Sharabi R, Markevich E, Borgel V, Salitra G, Aurbach D, Semrau G, Schmidt MA, Schall N, Stinner C (2011) *Electrochem Commun* 8:800
37. West WC, Whitacre JF, Ratnakumar BV (2003) *J Electrochem Soc* 150:1660
38. Bramnik NN, Bramnik KG, Baehtz C, Ehrenberg H (2005) *J Power Sources* 145:74
39. Lloris JM, Vicente CP, Tirado JL (2002) *Electrochem Solid State Lett* 5:234
40. Li HH, Jin J, Wei JP, Zhou Z, Yan J (2009) *Electrochem Commun* 11:95
41. Liu J, Conry TE, Song XY, Yang L, Doeff MM, Richardson TJ (2011) *J Mater Chem* 21:9984
42. Shui JL, Yu Y, Yang XF, Chen CH (2006) *Electrochem Commun* 8:1087
43. Han DW, Kang YM, Yin RZ, Song MS, Kwon HS (2009) *Electrochem Commun* 11:137
44. Wang F, Yang J, Nuli Y, Wang J (2010) *J Power Sources* 195:6884
45. Sun Q, Luo JY, Fu ZW (2011) *Electrochem Solid State Lett* 14:151
46. Wang F, Yang J, Nuli YN, Wang JL (2011) *J Power Sources* 196:4806
47. Doan TNL, Taniguchi I (2011) *J Power Sources* 196:5679
48. Yang JS, Xu JJ (2006) *J Electrochem Soc* 153:716
49. Jang IC, Son CG, Yang SMG, Lee JW, Cho AR, Aravindan V, Park GJ, Kang KS, Kim WS, Cho WI, Lee YS (2011) *J Mater Chem* 21:6510
50. Bramnik NN, Bramnik KG, Buhrmester T, Baehtz C, Ehrenberg H, Fuess H (2004) *J Solid State Electrochem* 8:558
51. Koleva V, Zhecheva E, Stoyanova R (2010) *Eur J Inorg Chem* 26:4091
52. Bramnik NN, Nikolowski K, Baehtz C, Bramnik KG, Ehrenberg H (2007) *Chem Mater* 19:908